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1. Your reference — 4/P32367GB

2. Patent application number *(The Patent Office will fill in this part)* — **9924722.3** — 19 OCT 1999

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

   SHIMADZU RESEARCH LABORATORY (EUROPE) LTD
   Wharfside
   Trafford Wharf Road
   Manchester M17 1GP

   Patents ADP number *(if you know it)* 7412 8000[1]

   If the applicant is a corporate body, give the country/state of its incorporation — UK

4. Title of the invention

   METHODS AND APPARATUS FOR DRIVING A QUADRUPOLE DEVICE

5. Name of your agent *(if you have one)*

   "Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

   MATHISEN, MACARA & CO
   The Coach House
   6-8 Swakeleys Road
   Ickenham
   Uxbridge UB10 8BZ

   Patents ADP number *(if you know it)* 1073001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

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Request for preliminary examination and search *(Patents Form 9/77)*	1
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11. I/We request the grant of a patent on the basis of this application.

Signature Mathisen Macara & Co
MATHISEN, MACARA & CO

Date 19 OCTOBER 199

12. Name and daytime telephone number of person to contact in the United Kingdom

M W BIBBY
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Patents Form 1/77

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Wharfside
Trafford Wharf Road
Manchester M17 1GP

Patents ADP number *(if you know it)* 74172 8000

If the applicant is a corporate body, give the country/state of its incorporation — UK

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Dated 18 OCT 2000

DUPLICATE

UK PATENT APPLICATION

APPLICANTS: SHIMADZU RESEARCH LABORATORY (EUROPE) LTD

SHORT TITLE: RECTANGULAR DRIVE

FORMAL TITLE: METHODS AND APPARATUS FOR DRIVING A QUADRUPOLE DEVICE

APPLICATION NO:

FILED:

PRIORITY CLAIMED:

MATHISEN, MACARA & CO.
The Coach House
6-8 Swakeleys Road
Ickenham, Uxbridge
Middlesex UB10 8BZ

AGENTS FOR THE APPLICANTS

METHODS AND APPARATUS FOR DRIVING A QUADRUPOLE DEVICE

This invention relates to quadrupole mass spectrometry. In particular, the invention relates to methods and apparatus for driving a quadrupole device, such as a linear quadrupole mass analyzer or an ion trap mass analyzer which, in the main, rely for their operation on a rotationally symmetric quadrupole electric field. The invention also relates to quadrupole devices using and incorporating said methods and apparatus.

The original idea of using a quadrupole mass analyzer and a quadrupole ion trap for mass analysis was first disclosed by W. Paul and H. Steinwedel in US Patent No. 2,939,952. Several different electrode geometries were described. These are mainly divided into two types; that is, the linear quadrupole structure and the 3D rotationally symmetric quadrupole ion trap structure, illustrated in Figures 1a and 1b respectively of the accompanying drawings. Referring to Figure 1a, the linear quadrupole structure includes a pair of x-electrodes 1, a pair of y-electrodes 2, an ion entrance 3 and an ion detector 4. Referring to Figure 1b, the quadrupole ion trap structure includes a ring electrode 1, and end cap electrodes 2,3, there being a central hole 4 in end cap electrode 2. To make these structures function as mass analyzers, a voltage having a periodic variation as a function of time needs to be applied across the electrodes. US Patent No. 2,939,952 teaches a method of generating a sinusoidal high frequency voltage combined with a DC voltage to achieve this periodic voltage. Upon application of such a voltage a quadrupole electric

field that drives the ions' motion is set up. The theory of ion motion based on the solution of Mathieu's equation was established. This theory has been widely used by others in later developments of quadrupole mass spectrometry and introduced in the related text book "Quadrupole Storage Mass Spectrometry" by E. March, R.J. Hughes, Wiley - Interscience Publication where the sinusoidal high frequency voltage is usually referred to as a radio frequency (RF) voltage.

Theories such as the pseudo potential well approximation for dealing with the motion of ions in a sinusoidal voltage-driven quadrupole field were further developed, and this led to many technological advances in the 1980's. Among these, resonant ejection using bipolar excitation disclosed in US patent Nos. 4,749,860 and 4,736,101 led to significant improvements in the performance of a quadrupole ion trap mass spectrometer enabling the device to carry out high resolution tandem mass analysis (MS^n).

Different scanning modes as well as the method of detection by Fourier transform of image current disclosed in US Patent No. 5,629,186 were then developed using these theories. These developments have brought about tremendous applications in mass spectrometry and in the combination of mass spectrometry with other widely used instrumentation.

Because, fundamentally, this technology is based on ion motion in the superimposed RF and DC quadrupole electric fields, or in some cases in a pure RF electric field, all

applications need an RF power source to supply RF voltage to the quadrupole devices. Conventionally, a RF power supply comprises a driving electric circuit and a resonating network which includes the quadrupole ion optical device as a load. The resonant frequency of the network is normally fixed or has a small number of fixed values. To achieve mass scanning or mass selection, the output voltage of the RF power supply must be able to ramp up and down precisely according to the desired scheme, the amplitude of the RF voltage being proportion to mass when the RF frequency is fixed. In some cases, a high RF voltage is necessary for high mass analysis. Also, sometimes an undesirable shift in the resonance position of the network caused by a change in output voltage needs to be corrected. These factors have resulted in increased costs and complexity of instruments.

A paper entitled "Frequency Scan for the Analysis of High Mass Ions Generated by Matrix-assisted Laser Desorption/Ionization in a Paul Trap" by U.P. Schlunegger et al, Rapid. Commun. Mass. Spectrom. 13, 1792-1796 (1999) discloses use of a frequency scanning technique instead of a voltage scanning technique to improve the mass scanning range of a quadrupole ion trap of a MALDI ion trap spectrometer. A waveform generator and a power amplifier were used to provide the frequency-variable sine wave voltage. This voltage output is limited by the power consumption of the amplifier which is basically an analogue circuit and has to work in a linear state. Therefore, when a higher trapping RF voltage is needed, it is difficult to reduce the power consumption, and so the machine size and production cost with this configuration.

In fact, it is not necessary to use a sinusoidal RF voltage to drive a quadrupole ion trap or a quadruople mass analyzer as was stated by W. Paul et al in US Patent No. 2,939,952. However, no practical method has been disclosed for high performance mass-selective operation within a quadrupole device driven by a waveform other than a sinusoidal waveform. Also, a method that allows mass scanning to be fully digitally controlled is desirable.

The method of this invention utilizes a time-varying rectangular wave voltage applied to a quadrupole device for ion trapping, selection, and/or mass analyzing.

According to one aspect of the invention there is provided a method for driving a quadrupole device including alternately switching between a high voltage level and a low voltage level to generate a time-varying rectangular wave voltage, and supplying said time-varying rectangular wave voltage to the quadrupole device to create therein a time-varying quadrupole electric field.

According to another aspect of the invention there is provided a method for driving a quadrupole device including supplying to the device a time-varying rectangular wave voltage to create therein a time-varying quadrupole electric field, and further supplying to the quadrupole device a time-varying bipolar excitation voltage to cause resonant oscillatory motion of ions in the device.

According to a further aspect of the invention there is provided an apparatus for driving a quadrupole device including means for alternately switching between a high voltage level and a low voltage level to generate a time-varying rectangular wave voltage and for supplying said time-varying rectangular wave voltage to the quadrupole device to create therein a time-varying quadrupole electric field.

According to a yet further aspect of the invention there is provided an apparatus for driving a quadrupole device including means for supplying to the device a time-varying rectangular wave voltage to create therein a time-varying quadrupole electric field, and means for further supplying to the device a time-varying bipolar excitation voltage to cause resonant oscillatory motion of ions in the device.

The said quadrupole device may be an ion optics system in a form of linear quadruople mass analyzer or a 3D rotationally symmetric quadrupole ion trap or any other electrode structure that can be used to generate a quadruople electric field for storing and/or mass analyzing ions.

Embodiments of the invention are now described, by way of example only, with reference to the accompanying drawings of which:

Figure 1a shows a known linear quadrupole structure,

Figure 1b shows a known 3-D rotationally-symmetric quadruople ion trapping structure,

Figure 2 shows a time-varying rectangular wave voltage in accordance with the invention,

Figure 3 is a block schematic diagram showing a drive apparatus according to the invention for use in a quadrupole ion trap,

Figure 4 shows the characteristics of ion motion in a quadrupole ion trap driven by different rectangular wave voltages, and

Figure 5 illustrates the stable region (shown hatched) in a plot of a against q for ion motion in the z-direction only.

The rectangular wave voltage shown in Figure 2 has a width w_1 at a high voltage level V_1 and a width w_2 at a low voltage level V_2. In this example, the rectangular wave voltage has a DC offset U given by:

$$U=(w_1V_1+w_2V_2)/(w_1+w_2) \tag{1}$$

and a repetition rate f given by:

$$f=(w_1+w_2)^{-1} \tag{2}$$

Figure 3 shows a drive apparatus for generating the rectangular wave voltage of Figure

2. The drive apparatus includes a clock 11 for generating a high frequency, high precision clock signal 12. A count unit 13 has a number of counters (the number e.g. 2 depending on the complexity of the required rectangular wave pattern) and an output gate for counting the clock pulses and setting or resetting the output gate according to a preset number of counts N_{w1},N_{w2} which determine the widths w_1,w_2 of the rectangular wave pattern. A mass scan control unit 14 which sets the counts N_{w1},N_{w2} is programmed to control the rectangular wave pattern and its variation during mass scanning.

The resultant pulse train 15 having the required pulse pattern is then supplied to a switch circuit including a normally closed switch 16 and a normally open switch 17. An adaption circuit between the count unit 13 and the switches 16,17 may be needed to overcome possible potential differences between the switches and to ensure that the switches operate at the required speed. Switch 16 is connected to a low level DC power supply 19 (V_2) and switch 17 is connected to a high level DC power supply 18 (V_1). When switches 16,17 are alternately opened and closed the high and low level voltages V_1,V_2 which form the rectangular wave drive voltage will be supplied to the quadrupole device.

In the case of a quadrupole device in the form of a quadrupole ion trap, the rectangular wave voltage is supplied to the ring electrode 20, and the end cap electrodes 21 may be connected to ground or alternately to a fixed DC bias voltage.

In the case of a quadrupole device having a linear quadrupole structure, the rectangular wave voltage is supplied to one pair of diagonally opposed electrodes and when a four pole device is used, another pair of diagonally opposed electrodes is driven by a second, identical switch circuit, but with the voltage sources 18,19 having opposite polarity.

As will be described in greater detail hereinafter, in accordance with one aspect of the invention the quadrupole device may be supplied with a time-varying, bipolar excitation voltage in addition to the time-varying rectangular wave drive voltage, the additional excitation voltage being effective to cause resonant oscillatory motion of ions in the quadrupole device. To this end, the drive apparatus is provided with a bipolar, AC excitation voltage source 22.

In the case of a quadrupole device in the form of a quadrupole ion trap, the additional voltage source 22 is connected between the end cap electrodes 21 whereas in the case of a quadrupole device having a linear quadrupole structure the additional voltage source is connected between one pair of diagonally opposed electrodes.

The bipolar excitation voltage may have a range of different AC waveforms, such as a single sinusoidal waveform, a rectangular waveform or a broad-band multi frequency waveform.

The repetition rate f of the rectangular wave drive voltage generated by the drive

apparatus of Figure 3 is related to the clock frequency f_{cl} and the preset number of counts N_{w1}, N_{w2} by the expression:

$$f=(w_1+w_2)^{-1}=f_{cl}(N_{w1}+N_{w2})^{-1}$$

In the simplest case, for which the rectangular wave voltage has a square waveform (i.e. $V_1 = -V_2 = V$, $w_1/w_2 = 1$), the DC power supply 19 may be set at a voltage having the same voltage as, but opposite polarity to, that of DC power supply 18. Alternatively, only a single DC power supply 18 is used and switch 16 is simply connected to ground. In this case, the resultant DC voltage offset can be cancelled out by applying a DC bias voltage $V_1/2$ to both end caps or by capacitively coupling the output voltage to the ring electrode 20 to isolate the DC offset.

In the case of a quadrupole device driven by a rectangular wave voltage, ion motion cannot be solved by Mathieu's equation which is fundamental to the afore-mentioned earlier theories of quadrupole mass spectrometry.

However, ion motion in a quadrupole field generated by a time-varying rectangular wave voltage can be defined by applying Newton's equation in different time segments. Within each segment the electric field is constant and so the equation can be easily solved.

The following is a brief illustration of an example of a theoretical derivation of ion motion.

Here, a square waveform or a symmetric rectangular waveform of the form shown in Figure 2 is applied to a standard quadrupole ion trap $(r_0 = \sqrt{2} z_0)$. For ease of illustration, it will be assumed that the waveform has no DC offset, so that V1 = -V2 = V, and it will also be assumed that $w_1/w_2=1$. This means that a voltage alternating between constant values of +/-V will be applied to the ring electrode of the ion trap during each half cycle. An ion's motion in the z direction is thus governed by the following differential equation: (Motion in r direction can be derived using a similar method, the two motions being independent)

$$\ddot{z} = \pm \frac{2eV}{r_0^2 m} z \tag{3}$$

A precise solution can be obtained both for the positive half cycle:

$$z = Ce^{\lambda t} + De^{-\lambda t} \tag{4a}$$

and for the negative half cycle:

$$z = G\cos(\lambda t) + H\sin(\lambda t) \quad , \tag{4b}$$

where C,D,G,H can be derived from the condition at the start of the half cycle and $\lambda = \left(\frac{q_z}{2}\right)^{1/2} \Omega$. Here, $\Omega = 2\pi f$ represents the rectangular wave repetition rate and q_z has the same definition as for a conventional RF driven quadrupole ion trap for ease of comparison between the two types of motion i.e.

$$q_z = \frac{4eV}{m\Omega^2 r_0^2} \tag{5}$$

The trajectory of an ion can be calculated by alternatively using the two phase space transfer matrices:

$$\begin{bmatrix} z_{n+1} \\ \dot{z}_{n+1} \end{bmatrix} = \begin{bmatrix} ch(\lambda\pi/\Omega) & sh(\lambda\pi/\Omega)/\lambda \\ sh(\lambda\pi/\Omega)\lambda & ch(\lambda\pi/\Omega) \end{bmatrix} \begin{bmatrix} z_n \\ \dot{z}_n \end{bmatrix} \tag{6a}$$

for the positive half cycle, and

$$\begin{bmatrix} z_{n+1} \\ \dot{z}_{n+1} \end{bmatrix} = \begin{bmatrix} \cos(\lambda\pi/\Omega) & \sin(\lambda\pi/\Omega)/\lambda \\ -\sin(\lambda\pi/\Omega)/\lambda & \cos(\lambda\pi/\Omega) \end{bmatrix} \begin{bmatrix} z_n \\ \dot{z}_n \end{bmatrix} \tag{6b}$$

for the negative half cycle.

The curves shown in Figure 4 represent ion position as a function of time for motion in the z-direction obtained by numerical calculation based on the above matrix calculus. The curves referenced 1,2,3 in Figure 4 are for q_z=0.15, 0.3 and 0.6 respectively, and it is clear that these values are in the range for bounded (or stable) ion motion.

If the rectangular wave voltage has a DC offset the parameter a_z also takes the definition used for Mathieu's equation i.e. $a_z = -\frac{8eU}{m\Omega^2 r_0^2}$. The a-q stability diagram is plotted in Figure 5 for the case w_1/w_2=1 where the shaded areas indicate the values of a and q for which the motion of ions is stable. This shows that by applying the rectangular wave voltage, ions can be separated into ions undergoing stable motion and ions undergoing unstable motion enabling ions satisfying certain criteria to be stored inside the ion trap.

By varying the values of V,U and/or Ω it is possible to scan ions into and out of the region of stablity according to mass-to-charge ratio. However, an alternative, more favourable method for mass selection also exists. This method can be used particularly, though not exclusively, in the case of a quadrupole ion trap structure where ions have already been stored in the device using the rectangular wave quadrupole field. Although the detailed motion shown in Figure 4 is complex, a major oscillation frequency for each curve can be clearly seen. A further theoretical study based on this pseudopotential well effect shows that for smaller values of q_z the angular frequency ω_z of this oscillation for the square wave case can be expressed as:

$$\omega_z = \left[\frac{1}{\pi} \frac{\sqrt{q_z}}{\sqrt{2}} (\sin\beta ch\beta - \cos\beta sh\beta) \right]^{1/2} \Omega \quad , \qquad (7)$$

where $\beta = \left(\frac{q_z}{8} \right)^{1/2} \pi$.

Taking the third order approximation, this can be simplified to

$$\omega_z \approx 0.45345 q_z \Omega \qquad (8)$$

This frequency will be referred to as the intrinsic frequency of the ion motion. The oscillation at this frequency is caused by the integrated effect of the rectangular wave electric field, and its frequency is a function of mass-to-charge ratio and of the repetition rate of the driving rectangular wave voltage.

Therefore, according to one aspect of the present invention an additional bipolar excitation voltage is used to cause ions having a selected mass-to-charge ratio to resonant at the intrinsic frequency ω_z.

At resonance these ions can be selectively excited and even ejected from an ion trap to be detected by an external detector. The resonant excitation also increases the kinetic energy of the selected ions and may promote certain chemical reactions or induce image current for Fourier transform detection.

One implementation of this resonance effect is now described by way of example using a conventional quadrupole ion trap having holes in one or both end caps. The excitation AC voltage can be a single frequency, sinusoidal voltage or a rectangular wave voltage or a waveform composed of multi-frequency components. When this voltage is applied between the two end-caps and one of its frequency components ω_0 approaches ω_z, ion motion in the z direction will be resonantly excited. The oscillation amplitude of the resonant ions will increase until the ions reach the end-cap electrodes or are ejected through the end-cap holes. Because the intrinsic frequency ω_z is a function of mass m, repetition rate f and the voltages defining the rectangular wave voltage, mass scanning using the desired resonance technique can be implemented in a variety of different ways:

1. Fix the repetition rate f of the driving rectangular waveform and scan the excitation frequency ω_0 e.g. from 0 to πf.

2. Use a digital frequency divider to make the excitation frequency ω_0 proportional to f, thereby fixing the value of q_z and scan the repetition rate f. The repetition rate f can be varied by increasing or decreasing the values of N_{w1} and N_{w2}.

3. Fix the excitation frequency ω_0 and scan the repetition rate f of the rectangular wave voltage by gradually increasing or decreasing the values of the preset number of counts N_{w1}, N_{w2}. From equations (8) and (5) above it can be seen that

$$\frac{m}{e}=\frac{1.814V}{r_0^2\omega_0}\Omega^{-1}\propto(N_{w1}+N_{w2}) \ , \qquad (9)$$

indicating that the mass scan can be made approximately linear by linearly increasing the preset number of counts N_{w1},N_{w2} which digitally control the repetition rate of the rectangular wave voltage.

Although the above derivation is for a symmetric rectangular wave voltage where DC offset is zero, it will be appreciated that a finite DC offset and other waveform patterns are also within the scope of the invention. Although the voltages of the driving rectangular waveform were fixed during mass scanning, different mass scanning ranges can be obtained by using different voltages. Application of the rectangular wave voltage to drive the motion of ions in combination with broad band excitation where the frequency range is determined using equations (7) or (8) is also within the scope of the

invention.

In the case of broad band excitation, a broad band waveform generator can still be used as was taught in US Patent Nos. 5134286 and 4761545.

In general, the rectangular wave voltage driven quadrupole mass spectrometry has the following merits compared with the current RF driven quadrupole mass spectrometry.

The rectangular wave voltage may be generated using a switching circuit which does not employ a LC resonator and so the frequency or the wave repetition rate can be easily changed. A practical range may be from 10kHz to 10MHz. It is known from the characteristics of ion motion in the quadrupole electric field that the range of mass scanning is made wider by varying frequency than by varying voltage within certain practical limits (for example discharge at high voltage).

A rectangular waveform can be defined using more parameters than is the case for a sinusoidal waveform. These parameters provide more options for storing and manipulating ions. For example, the rectangular waveform pattern can easily be changed intermittently or temporarily during which time the ions from an external ion source can be introduced into the quadrupole device.

A switching circuit used to generate a rectangular wave voltage consumes less power than

an untuned analogue circuit used to generate an RF drive voltage. This leads to a reduction in the power specificaton of the associated electronics.

There is currently a large number of advanced digital switching devices that will enable a rectangular waveform be generated with high precision and low cost. While the miniature or 'on chip' quadrupole mass analyzer or ion trap are under the development, a highly integrated drive circuit is also demanded. Using a fully digital driving voltage to define a rectangular wave voltage can reduce circuit complexity and minimize the size and the cost of the device as well as the total cost of the instrument.

CLAIMS

1. A method for driving a quadrupole device including:

alternately switching between a high voltage level and a low voltage level to generate a time-varying rectangular wave voltage, and supplying said time-varying rectangular wave voltage to the quadrupole device to create therein a time-varying quadrupole electric field.

2. A method as claimed in claim 1 including digitally controlling said switching.

3. A method as claimed in claim 2 including generating clock pulses, counting said clock pulses and causing said switching according to the value the count.

4. A method as claimed in claim 3 including switching between said high and low voltage levels when the count reaches respective preset values.

5. A method as claimed in any one of claims 1 to 4 wherein said time-varying rectangular wave voltage is defined by said high voltage level V_1, said low voltage level V_2 and the respective time widths w_1 and w_2 of said rectangular wave voltage at said high and low voltage levels V_1 and V_2, and including varying one or more of said parameters V_1, V_2, w_1, w_2 as a function of time whereby selectively to cause ions having different mass-to-charge ratios to undergo stable oscillatory motion within the quadrupole device.

6. A method as claimed in claim 5 including varying said one or more parameter to scan through a predetermined range of mass-to-charge ratio.

7. A method as claimed in any one of claims 1 to 6 wherein said time-varying rectangular wave voltage is a time-varying square wave voltage.

8. A method as claimed in any one of claims 1 to 7 wherein said time-varying rectangular wave voltage has a DC offset.

9. A method as claimed in any one of claims 1 to 8 wherein said time-varying rectangular wave voltage is periodic.

10. A method as claimed in any one of claims 1 to 9 including further supplying to the quadrupole device a time-varying bipolar excitation voltage whereby to excite resonant oscillatory motion of ions in the device.

11. A method as claimed in claim 10 including fixing one of the repetition rate of said time-varying rectangular wave voltage and the excitation frequency of said time-varying bipolar excitation voltage and varying another of said repetition rate and said excitation frequency whereby selectively to cause ions having different mass-to-charge ratios to undergo said resonant oscillatory motion.

12. A method as claimed in claim 10 wherein the repetition rate of said time-varying rectangular wave voltage and the excitation frequency of said time-varying bipolar excitation voltage have a fixed relationship and including scanning said repetition rate and said excitation frequency through a predetermined range whereby selectively to cause ions having different mass-to-charge ratios to undergo said resonant oscillatory motion.

13. A method as claimed in claim 11 or claim 12 including generating clock pulses, counting said clock pulses and causing said switching when the count reaches respective preset values, and wherein said repetition rate is determined by said preset values.

14. A method as claimed in any one of claims 10 to 13 wherein said time-varying bipolar excitation voltage is applied in order to extract ions from the quadrupole device.

15. A method as claimed in any one of claims 1 to 14 wherein the quadrupole device is a linear quadrupole mass analyzer.

16. A method as claimed in any one of claims 1 to 14 wherein the quadrupole device is an ion trap device for generating a quadrupole electric field.

17. A method as claimed in any one of claims 1 to 14 wherein the ion trap device generates a quadrupole electric field and higher order multipole electric fields.

18. A method for driving a quadrupole device including supplying to the device a time-varying rectangular wave voltage to create therein a time-varying quadrupole electric field, and further supplying to the quadrupole device a time-varying bipolar excitation voltage to excite resonant oscillatory motion of ions in the device.

19. A method as claimed in claim 18 including fixing one of the repetition rate of said time-varying rectangular wave voltage and the excitation frequency of said time-varying bipolar excitation voltage and varying another of said repetition rate and said excitation frequency whereby selectively to cause ions having different mass-to-charge ratios to undergo said resonant oscillating motion.

20. A method as claimed in claim 18 wherein the repetition rate of said time-varying rectangular wave voltage and the excitation frequency of said time-varying bipolar excitation voltage have a fixed relationship, and including scanning said repetition rate and said excitation frequency through a predetermined range whereby selectively to cause ions having different mass-to-charge ratios to undergo said resonant oscillating motion.

21. A method as claimed in claim 19 or claim 20 including generating clock pulses, counting said clock pulses and switching between high and low voltage levels to generate said rectangular wave voltage when the count reaches respective preset values, wherein the repetition rate is determined by said preset values.

22. An apparatus for driving a quadrupole device including:

means for alternately switching between a high voltage level and a low voltage level to generate a time-varying rectangular wave voltage and for supplying said time-varying rectangular wave voltage to the quadrupole device to create therein a time-varying quadrupole electric field.

23. An apparatus as claimed in claim 22 including means for digitally controlling the switching means.

24. An apparatus as claimed in claim 23 wherein the control means includes a source of clock pulses and means for counting said clock pulses and for causing said switching according to the value of the count.

25. An apparatus as claimed in claim 24 wherein said switching is effected when the count reaches respective preset values.

26. An apparatus as claimed in any one of claims 22 to 25 wherein said time-varying rectangular wave voltage is defined by said high voltage level V_1, said low voltage level V_2 and the respective time widths w_1 and w_2 of said rectangular wave voltage at said high and low voltage levels, and including means for varying one or more of said parameters V_1, V_2, w_1, w_2 as a function of time whereby selectively to cause ions having different mass-to-charge ratios to undergo stable oscillatory motion within the quadrupole device.

27. An apparatus as claimed in claim 26 wherein said means for varying scans through a predetermined range of mass-to-charge ratios.

28. An apparatus as claimed in any one of claims 22 to 26 wherein said time-varying rectangular wave voltage is a time-varying square wave voltage.

29. An apparatus as claimed in any one of claims 22 to 28 wherein said time-varying rectangular wave voltage has a DC offset.

30. An apparatus as claimed in any one of claims 22 to 29 wherein said time-varying rectangular wave voltage is periodic.

31. An apparatus as claimed in any one of claims 22 to 30 including means for supplying to the quadrupole device a time-varying bipolar excitation voltage whereby to excite resonant oscillatory motion of ions in the device.

32. An apparatus as claimed in claim 31 including means for fixing one of the repetition rate of said time-varying rectangular wave voltage and the excitation frequency of said bipolar excitation voltage and varying another of said repetition rate and said excitation frequency whereby selectively to cause ions having different mass-to-charge ratios to undergo said resonant oscillatory motion.

33. An apparatus as claimed in claim 31 wherein the repetition rate of said time-varying rectangular wave voltage and the excitation frequency of said bipolar excitation voltage have a fixed relationship and including means for scanning said repetition rate and said excitation frequency through a predetermined range whereby selectively to cause ions having different mass-to-charge ratios to undergo said resonant oscillatory motion.

34. An apparatus as claimed in claim 32 or claim 33 including a source of clock pulses and means for counting clock pulses and for causing said switching when the count reaches respective preset values, and said repetition rate is determined by said preset values.

35. An apparatus for driving a quadrupole device including:

means for supplying to the device a time-varying rectangular wave voltage to create therein a time-varying quadrupole electric field, and

means for further supplying to the device a time-varying bipolar excitation voltage to excite resonant oscillatory motion of ions in the device.

36. An apparatus as claimed in claim 35 including means for fixing one of the repetition rate of said time-varying rectangular wave voltage and the excitation frequency of said time-varying bipolar excitation voltage and varying another of said repetition rate and said excitation frequency whereby selectively to cause ions having different mass-to-charge ratios to undergo said resonant oscillatory motion.

37. An apparatus as claimed in claim 35 wherein the repetition rate of said time-varying rectangular wave voltage and the excitation frequency of said time-varying bipolar excitation voltage have a fixed relationship, and including means for scanning said repetition rate and said excitation frequency through a predetermined range whereby selectively to cause ions having different mass-to-charge ratios to undergo said resonant oscillatory motion.

38. An apparatus as claimed in claim 36 or claim 37 including a source of clock pulses, means for counting the clock pulses and means for switching between high and low voltage levels to generate said rectangular wave voltage when the count reaches respective preset values, and wherein said repetition rate is determined by said preset values.

39. A quadrupole mass spectrometer including an apparatus as claimed in any one of claims 22 to 37.

40. A quadrupole mass spectrometer as claimed in claim 39 including a linear quadrupole mass analyzer.

41. A quadrupole mass spectrometer as claimed in claim 39 including an ion trap device having a ring electrode and end-cap electrodes, wherein said time-varying rectangular wave voltage is supplied to the ring electrode.

42. A quadrupole device as claimed in claim 40 wherein said linear quadrupole analyzer is a four pole analyzer and a first said time-varying rectangular wave voltage is applied to a one pair of diagonally opposed electrodes and a second said time-varying rectangular wave voltage having opposite polarity is applied to another pair of diagonally opposed electrodes.

43. A method as claimed in claim 8 including removing said DC offset.

44. An apparatus as claimed in claim 29 including means for removing said DC offset.

45. An apparatus as claimed in claim 44 wherein the removal means comprises capacitive means, said rectangular wave voltage being supplied to the quadrupole device via said capacitive means whereby to isolate said DC offset.

46. An apparatus as claimed in claim 44 wherein the removal means comprises means for supplying a DC bias voltage to the end caps of an ion trap device to cancel said DC offset.

47. A method for driving a quadrupole device substantially as hereindescribed with reference to Figures 2 to 5 of the accompanying drawings.

48. An apparatus for driving a quadrupole device substantially as hereindescribed with

reference to Figures 2 to 5 of the accompanying drawings.

ABSTRACT

METHODS AND APPARATUS FOR DRIVING A QUADRUPOLE DEVICE

A drive apparatus (Figure 3) for a quadrupole device such as a quadrupole ion trap has a switching arrangement (17,18) which alternately switches between high and low voltage levels (V_1,V_2) to generate a rectangular wave drive voltage. A bipolar excitation voltage is also supplied to the quadrupole device to excite resonant oscillatory motion of ions.

Fig. 1a

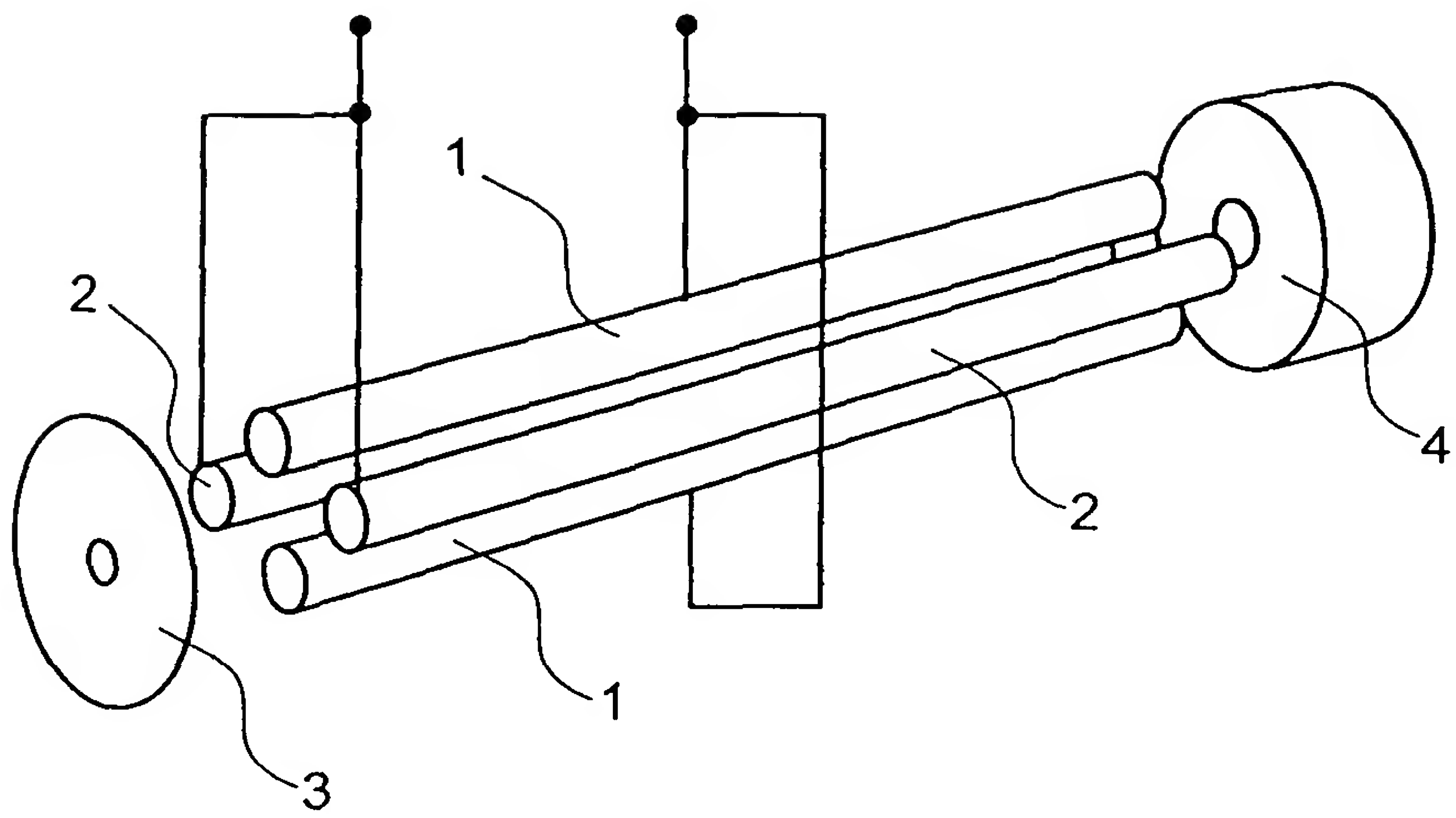
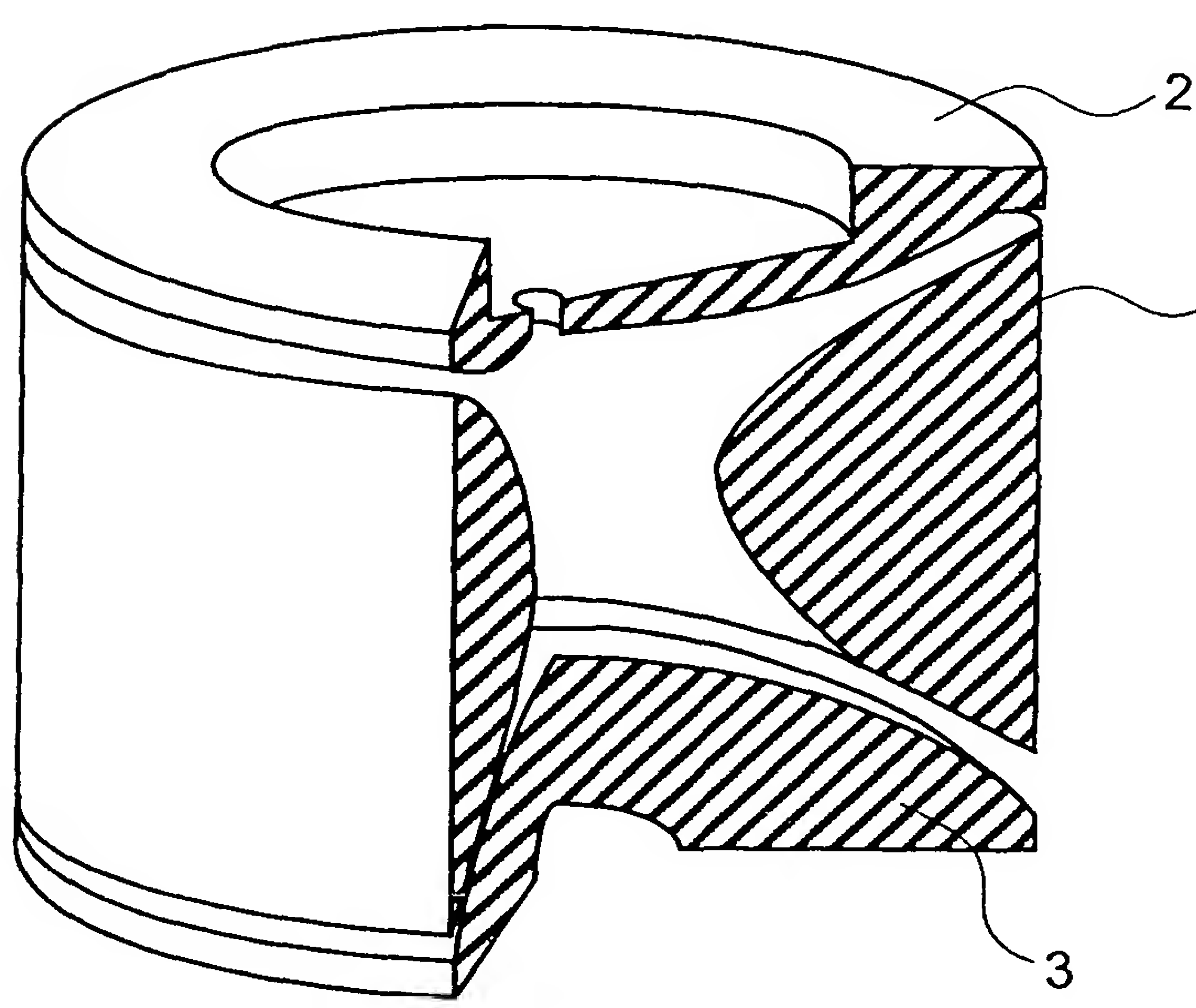


Fig. 1b



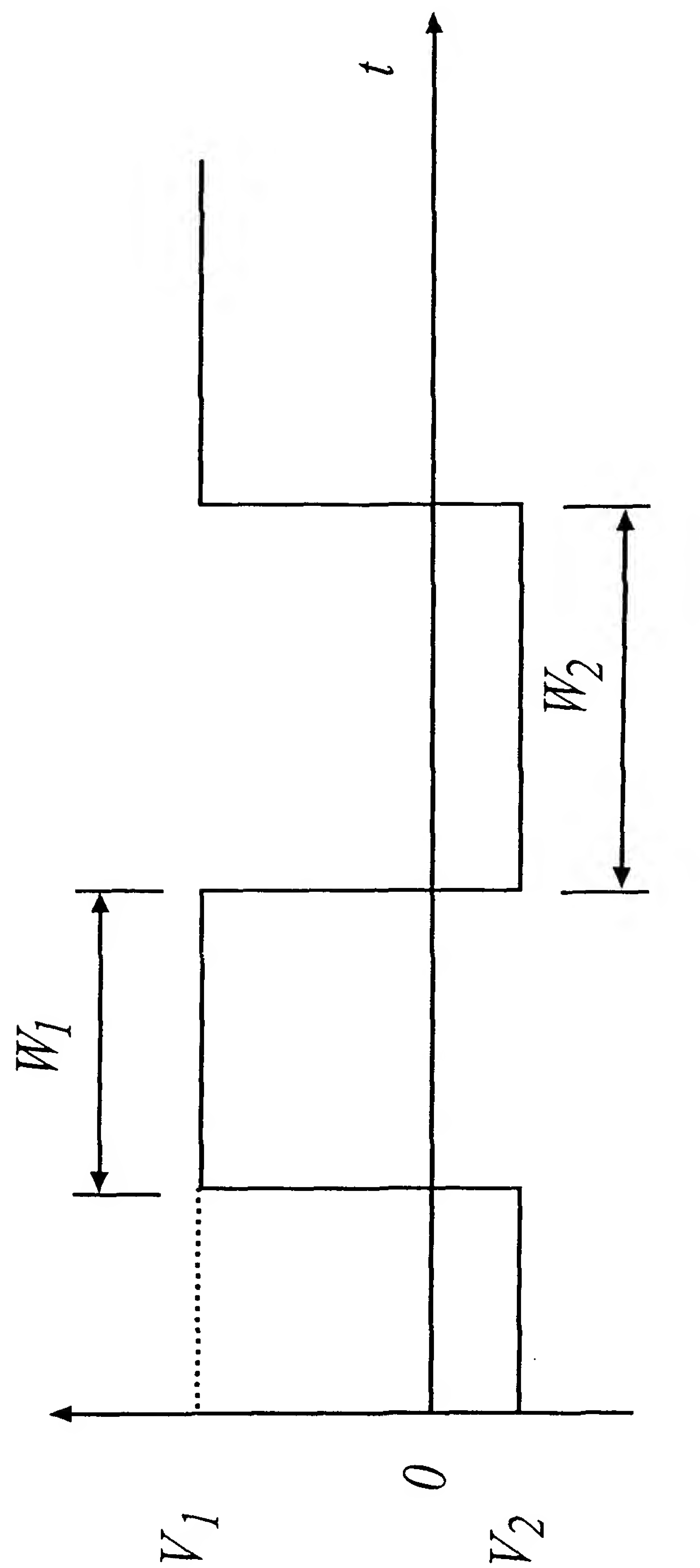
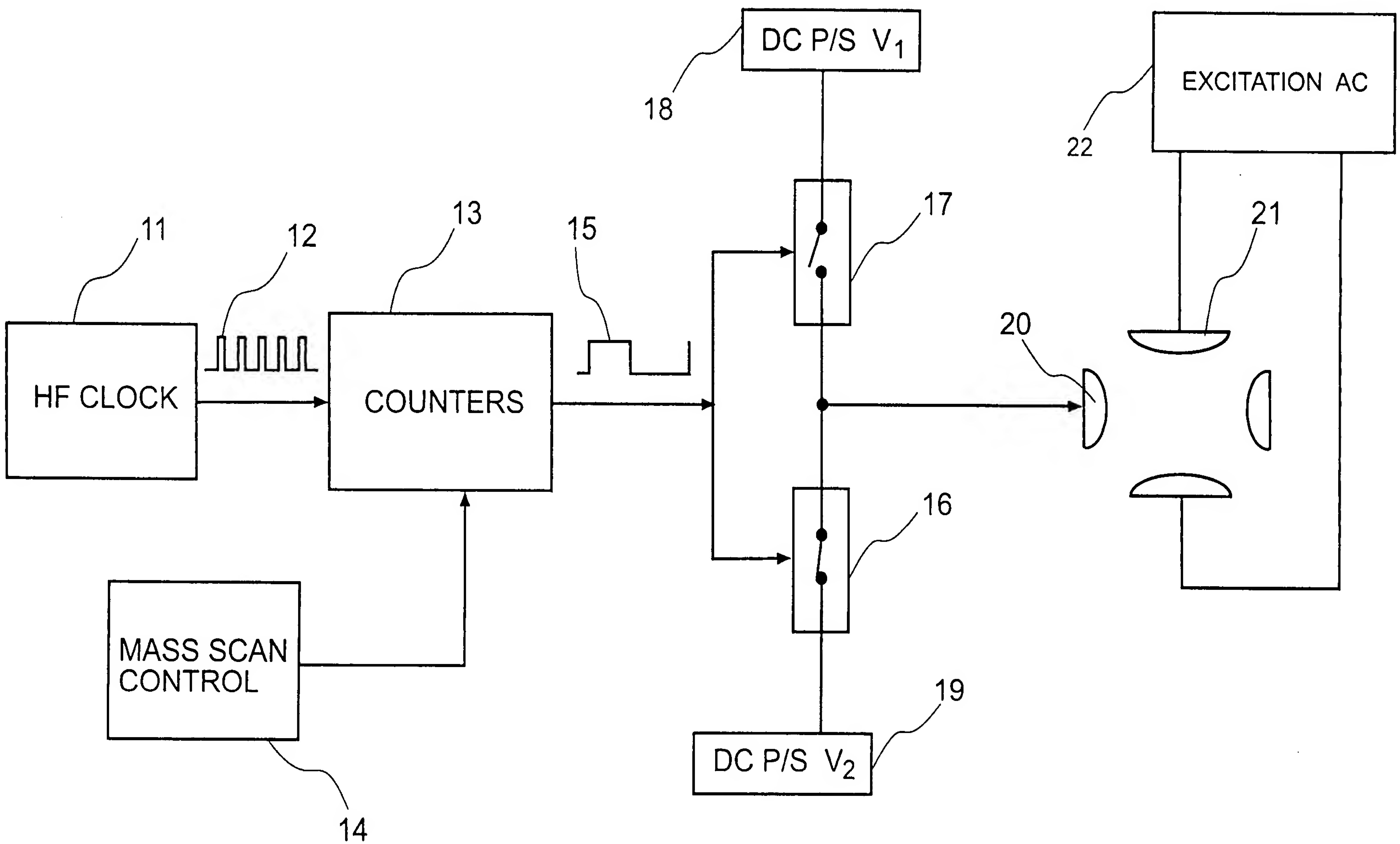


Fig. 2

Fig. 3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11
12
COUNTERS
13
15
MASS SCAN CONTROL
14
DC P/S V_1
18
17
16
DC P/S V_2
19
20
21
EXCITATION AC
22

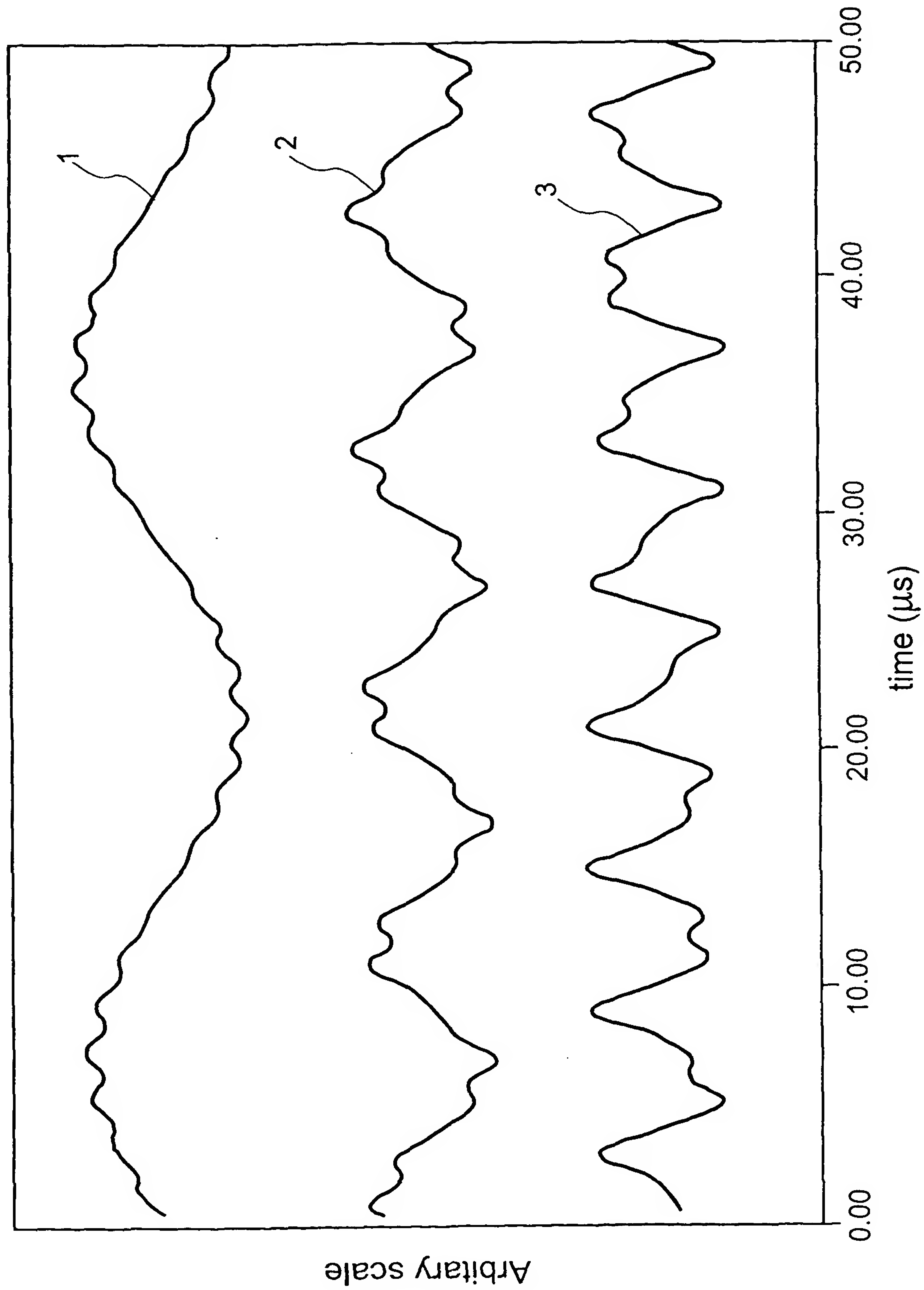

Fig. 4